Organic Chemistry

RADICAL REACTIONS USING POLARITY REVERSAL CATALYSIS

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Currently, radical reductions of alkyl bromides are performed with the use of tributyltinhydride, which is quite harmful to the environment. Roberts developed polarity reversal catalysis as a way to reduce alkyl bromides using bulky thiols and silanes instead of toxic trialkyltin reagents. Polarity reversal catalysis uses a thiol to enhance the rate of the hydrogen transfer from silanes which is usually slow. Unfortunately, the synthetic usefulness of polarity reversal catalysis is limited since the reactions fail in the presence of carbon-carbon double bonds due to side reactions between the thiol and the carbon-carbon double bond. We have found that the use of bulkier thiols, such as 3-ethyl-3-pentanethiol, and silanes, such as triispropylsilane, avoid some of these side reactions.

The reduction of octyl bromide in the presence of 3-ethyl-3-pentanethiol and triispropylsilane gave octane in high yields. Conditions for the reduction of octyl bromide to octane were optimized by altering the amount of initiator, thiol concentration, and reaction time. After demonstrating polarity reversal catalysis worked to reduce alkyl bromides, the radical cyclization of 6-bromohexene to methylcyclopentane was examined using bulky thiols as catalysts. This type of cyclization reaction can be used to determine of the effectiveness of the thiol reacting with a compound containing a carbon-carbon double bond. In the presence of 3-ethyl-3-pentanethiol and triispropylsilane, yields of methylcyclopentane reached 77.5%. The lower yield is attributed to possible side reactions taking place between the carbon-carbon double bond and the 3-ethyl-3-pentanethiol. In an attempt to minimize these undesired reactions and increase the yield of methylcyclopentane, a bulkier thiol, 5-isopropyl-5-nonanethiol, has been synthesized and is being tested for its suitability as a polarity reversal catalyst.